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Ultraviolet stimulated emission and optical gain spectra in $\text{Cd}_x\text{Zn}_{1-x}\text{S-ZnS}$ strained-layer superlattices

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Stimulated emission at 374.9 nm has been observed in an optically pumped $\text{Cd}_{0.22}\text{Zn}_{0.78}\text{S-ZnS}$ strained-layer superlattice at room temperature. Using a pump-and-probe technique with nanosecond excitation pulses, optical gain has also been observed at the tail part of the $n=1$ heavy-hole exciton absorption spectrum in the presence of the clear absorption peak of the exciton. Our experimental results suggest that the stimulated emission originates from excitonic gain.

Much progress has recently been made in the application of wide-band-gap II-VI compound semiconductor heterostructures, especially those based on CdZnSe-ZnSe quantum well systems, for injection laser diodes^{1,2} and display devices^{3,4} operating in the blue-green region of the spectrum. It is through the successful development of doping techniques for p -type conductivity control that these device applications have been achieved. Furthermore, there has been much work on optically pumped laser operation in a variety of wide-band-gap II-VI multiple quantum well (MQW) structures and double heterostructures such as ZnSe-ZnMnSe ,⁵ CdZnSe-ZnSSe ,⁶ CdZnSe-CdZnSSe ,⁷ ZnSe-ZnSSe ,^{8,9} and CdZnTe-ZnTe .¹⁰ These studies have enabled us to understand the fundamental lasing characteristics of each of these systems.

Among wide-band-gap II-VI compound semiconductors with zincblende structures, ZnS has the largest band-gap energy (3.73 eV at room temperature), so that ZnS-based MQW structures exhibit fundamental absorption edges at the shortest wavelengths. Moreover, ZnS has a relatively large exciton binding energy of about 40 meV. Therefore, quasi-two-dimensional excitons in quantum wells may have very large binding energies due to the effect of the quantum confinement. In this letter, we demonstrate ultraviolet stimulated emission in optically pumped $\text{Cd}_x\text{Zn}_{1-x}\text{S-ZnS}$ strained-layer superlattices (SLSs) at room temperature (RT). This type of SLS has previously been proposed and fabricated by Endoh *et al.*¹¹⁻¹³ We also present optical gain spectra for this SLS measured by means of a pump-and-probe technique employing nanosecond excitation pulses. These experimental results suggest that the origin of optical gain is different from that of III-V MQW systems in which an electron-hole plasma plays a principal role in providing gain.

Cubic-structured $\text{Cd}_x\text{Zn}_{1-x}\text{S-ZnS}$ SLSs were grown by low-pressure metalorganic chemical vapor deposition (MOCVD) using all gaseous sources on (100)-oriented GaAs substrates, following the deposition of a 1.5- μm -thick ZnS buffer layer. The MQW structures used in this study consist of 50 periods of 4.1-nm thick $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ well layers separated by 8.1-nm thick ZnS barrier layers. The Cd composition ratio in the ternary alloy well layer was

varied from $x=0.11$ to $x=0.49$. In this case, the ternary alloy well layers are under biaxial compression and the lattice mismatch between the well and barrier layers varies from approximately 0.8% to 3.8%. The individual well and barrier layers are believed to be within the critical layer thickness because the critical layer thickness of a ZnSe-ZnS SLS with a large lattice mismatch of about 4.5% has been determined to be about 10 nm by transmission electron microscopy.¹⁴

Figure 1 shows absorption (solid lines) and photoluminescence (dashed lines) spectra at 10 K taken from $\text{Cd}_x\text{Zn}_{1-x}\text{S-ZnS}$ SLSs with various Cd composition ratios in the ternary alloy well layer ($a:x=0.11$, $b:x=0.22$, $c:x=0.31$, $d:x=0.42$, and $e:x=0.49$). The absorption spectra were measured after removal of the GaAs substrate by chemical etching. The photoluminescence (PL) spectra were obtained under weak excitation using a continuous-wave He-Cd laser (325 nm). It can be seen from this figure that the effective band-gap energy of this type of SLS varies widely within the ultraviolet spectral region according to the composition x of the $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ well layer. Moreover, this type of SLS exhibits a strong excitonic emission band even at room temperature. The band lineup of this type of SLS has been found to always be type I on the basis of our semiquantitative calculations that modify the model-solid theory¹⁵ and photoluminescence excitation (PLE) measurements.¹⁶ The dominant excitonic emission band in each SLS shown in Fig. 1 is attributable to radiative recombination of $n=1$ heavy-hole excitons localized at interface and compositional fluctuations in the ternary alloy well layer. With increasing Cd mole fraction x , the Stokes shift becomes larger as well as the linewidth of both the absorption and emission spectra. This may be due to increases in interface fluctuations, compositional fluctuations, and the lattice mismatch strain. However, the dominant cause is not clearly understood at the present time.

The samples mentioned above were cleaved to approximately 1-mm long resonators with uncoated facets and excited perpendicular to the MQW layer plane. The excitation source was a frequency-tripled Q -switched $\text{Nd}^{3+}:\text{YAG}$ laser (355 nm). The pulse width was approximately 5 ns and the repetition rate was 30 Hz. We also

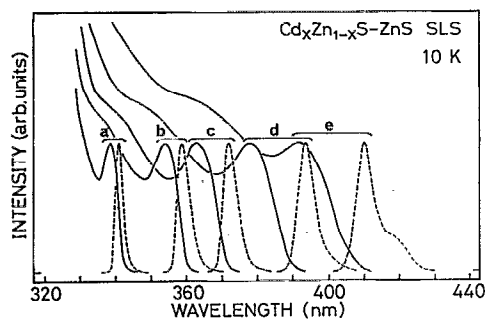


FIG. 1. Absorption (solid lines) and photoluminescence (dashed lines) spectra taken from $\text{Cd}_x\text{Zn}_{1-x}\text{S-ZnS}$ SLSs at 10 K with various Cd composition rates in the ternary alloy well layer ($a: x=0.11$, $b: x=0.22$, $c: x=0.31$, $d: x=0.42$, and $e: x=0.49$).

employed a N_2 pulsed laser (337 nm, 3 ns, and 30 Hz) as the excitation source for the sample labeled *a* in Fig. 1. Edge emission from one of the facets of the sample was detected using an optical multichannel analyzer in conjunction with 1-m or 25-cm single grating monochromators. For the sample with a Cd composition of $x=0.22$ in the ternary alloy well layer, stimulated emission spectra (SE; dotted lines) observed from the cleaved facet at 10 K and RT are shown in Figs. 2(a) and 2(b), respectively. In this figure, absorption spectra (ABS; solid lines) and photoluminescence spectra (PL; dashed lines) observed from the front face of the sample are also shown. The peak position of the stimulated emission is located at 361.2 nm at 10 K and is shifted to 374.9 nm at RT. Figure 3 shows the edge emission intensity at 10 K, 80 K, 150 K, 225 K, and RT as a function of excitation power density. The threshold excitation power density for stimulated emission is about 7 kW/cm^2 at 10 K. This value increases gradually with temperature, and the room-temperature threshold is

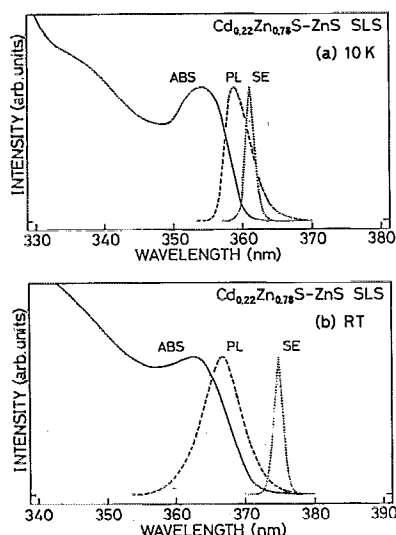


FIG. 2. Stimulated emission spectra (SE; dotted lines) from the edge facet of a $\text{Cd}_{0.22}\text{Zn}_{0.78}\text{S-ZnS}$ SLS at 10 K in (a) and at room temperature in (b). Absorption spectra (ABS; solid lines) and photoluminescence spectra (PL; dashed lines) from the front face of the sample at each temperature are also shown.

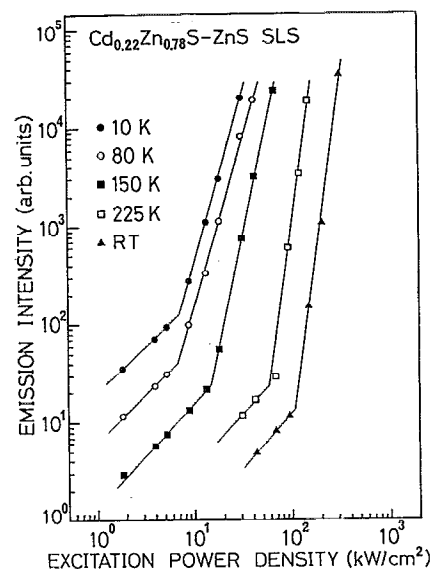


FIG. 3. Edge emission intensity of a $\text{Cd}_{0.22}\text{Zn}_{0.78}\text{S-ZnS}$ SLS as a function of the excitation power density at different temperatures.

about 110 kW/cm^2 . The conduction and valence band offsets in this sample have been estimated to be $\Delta E_c \approx 240 \text{ meV}$ and $\Delta E_v \approx 107 \text{ meV}$ (heavy-hole band), respectively, including the effects of the strain due to the lattice mismatch (1.7%).¹⁶ These values are thought to be sufficient to confine both electrons and heavy holes in the quasi-two-dimensional potential wells up to room temperature.

Recently, Ding *et al.* have reported that excitons play a central role in the formation of optical gain in the CdZnSe-ZnSe MQW structures.¹⁷ In order to study the mechanism of optical gain in our samples, pump-and-probe experiments with nanosecond excitation pulses were performed. The frequency-tripled Q -switched $\text{Nd}^{3+}:\text{YAG}$ laser mentioned above was used as a pump source. As a probe source, amplified spontaneous emission from Exalite 376 dye solution, excited by a portion of the pump source, was used. The probe pulse covered the spectral range from approximately 360 to 390 nm. The spot of the probe pulse on the sample was $200 \mu\text{m}$ in diameter and spatially centered in the excitation spot of the pump pulse which was 2 mm in diameter. The time delay between pump and probe pulses was adjusted to be zero. Figure 4 shows pump-and-probe absorption spectra taken from a $\text{Cd}_{0.31}\text{Zn}_{0.69}\text{S-ZnS}$ SLS at 10 K. The dashed line shows the absorption spectrum without the pump pulses while the solid line shows the spectrum with an excitation power density of approximately 253 kW/cm^2 . The inset shows enlarged spectra in the tail region of the excitonic absorption peak at excitation power densities of (a) 18, (b) 65, (c) 143, (d) 193, and (e) 253 kW/cm^2 . With increasing pump intensity, absorption around 375 nm gradually decreases. Above 143 kW/cm^2 , negative absorption is observed and this increases with pump intensity. This observation unambiguously indicates the presence of gain. The stimulated emission observed in this sample was naturally located at 374.9 nm at 10 K, and the threshold excitation power density was es-

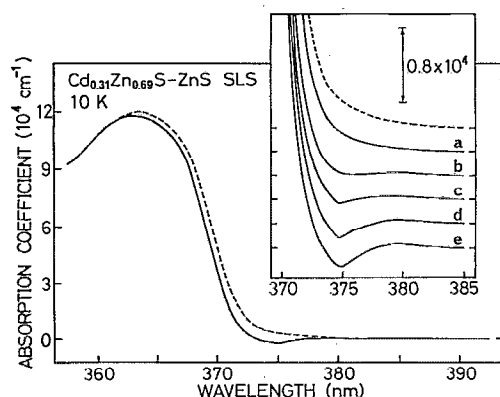


FIG. 4. Pump-and-probe absorption spectra taken from a $\text{Cd}_{0.31}\text{Zn}_{0.69}\text{S}$ -ZnS SLS at 10 K. The dashed line shows the absorption spectrum without the pump pulses. The solid line shows the spectrum with an excitation power density of about 253 kW/cm^2 . The inset shows the enlarged spectra at the tail part of the excitonic absorption peak at excitation power densities of (a) 18, (b) 65, (c) 143, (d) 193, and (e) 253 kW/cm^2 .

timated to be about 31 kW/cm^2 . The pump intensity at which negative absorption appears is several times larger than the threshold for stimulated emission. This is due to the inhomogeneous excitation over 50 quantum wells (QWs) along the growth direction. In fact, the transmittance of the excitation pulse through the 50 QWs is estimated to be about 20%. Several QWs near the surface of the sample dominantly contribute to the stimulated emission. On the other hand, all of the 50 QWs, on the average, contribute to the optical gain which is observed in the pump-and-probe configuration.

The main feature of our experimental findings is the observation of optical gain even in the presence of the clear excitonic absorption peak which is slightly bleached at the lower energy side. This result suggests that excitons contribute to the formation of optical gain and, moreover, there is no evidence for the presence of an electron-hole plasma. As for the mechanism of excitonic gain in quantum wells, the contribution of excitons themselves in inhomogeneous broadening,¹⁷ the contribution of localized excitons, or the contribution of excitonic molecules will be adopted. In order to elucidate this mechanism, more de-

tailed experimental and theoretical analyses are required and are currently underway.

In conclusion, ultraviolet stimulated emission has been demonstrated in optically pumped $\text{Cd}_{0.22}\text{Zn}_{0.78}\text{S}$ -ZnS SLS at room temperature. The stimulated emission observed in this study is characterized by the shortest wavelength (374.9 nm) reported to date in wide-band-gap II-VI MQW structures. It has also been suggested by pump-and-probe experiments that the mechanism of optical gain is due to the excitonic process.

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